

Plasma-Based Surface Modification and Corrosion in High Temperature Environments

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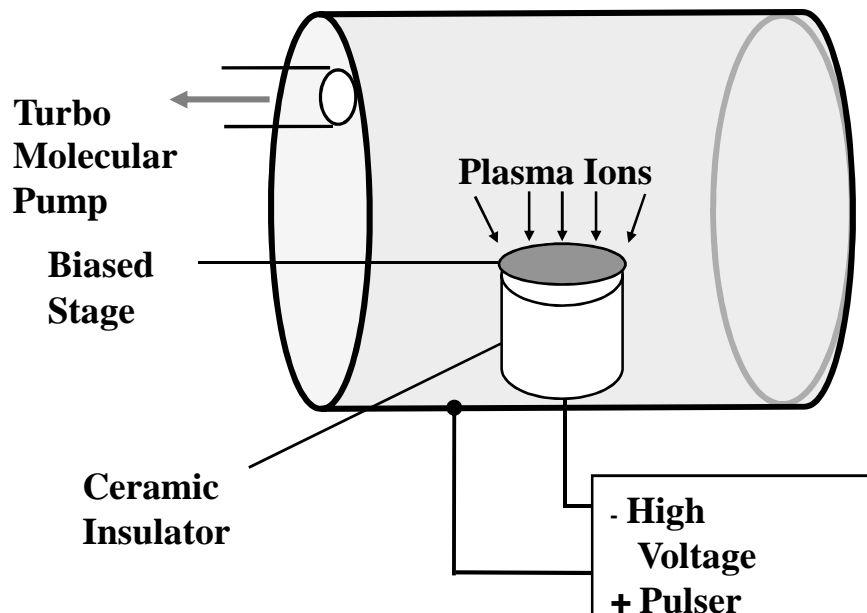
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Corrosion research at the University of Wisconsin, Madison

- Plasma Immersion Ion Implantation and Deposition (PIID), a non-line-of-sight surface treatment technology for improving wear and corrosion resistance of materials
- High temperature corrosion studies in harsh environments aimed at future nuclear reactors; materials corrosion research applicable to DoD applications



Plasma Immersion Ion Implantation and Deposition (PIIID)



- Vacuum chamber pumped down to 10^{-6} Torr using roughing and turbo pumps
- Gas containing surface modification species introduced
- Gas ionized to create a plasma
- Sample stage pulse biased to high negative potential
- Positive ions in the plasma accelerated to sample materials' surface at high velocities to change properties

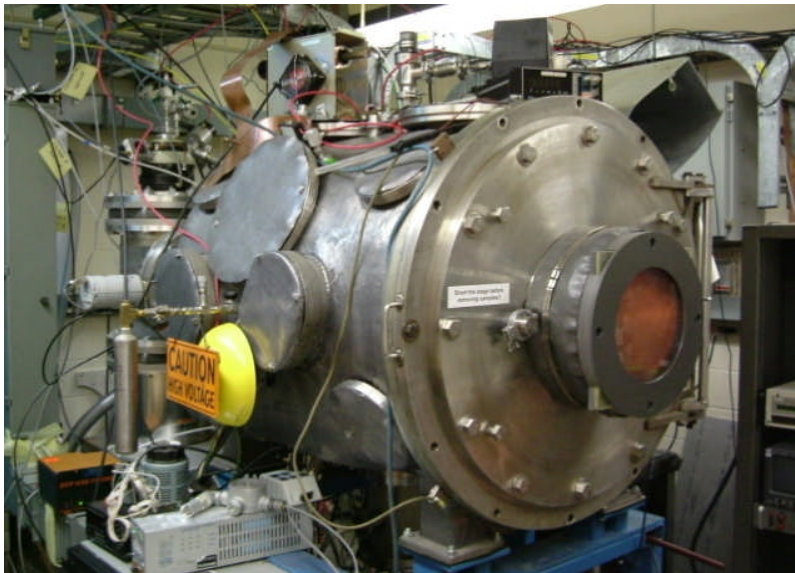


Types of PIIID surface treatments

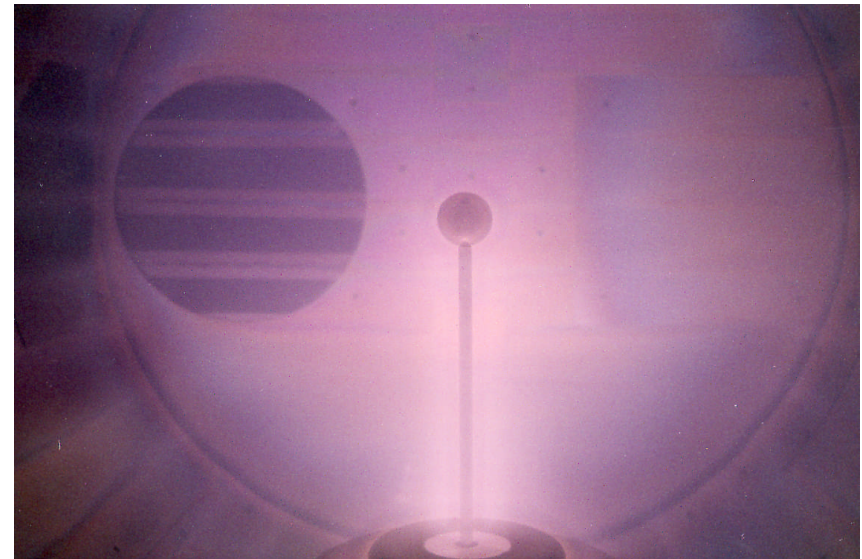
- Ion implantation of species from gaseous precursors (~50kV, N,O, Ar, C etc.)
- Coating deposition (e.g., wear-resistant, hydrophobic coatings such as diamond-like carbon (DLC) and Si-DLC, performed at < 5kV)
- Energetic ion mixing of thin nano-multilayers
- Enhancing coating-substrate adhesion by ion implantation prior to deposition
- Materials removal (e.g. environmentally benign plasma cleaning)
- Cross-linking thin polymer coatings for mechanical strength



PIID process system and picture of a nitrogen plasma

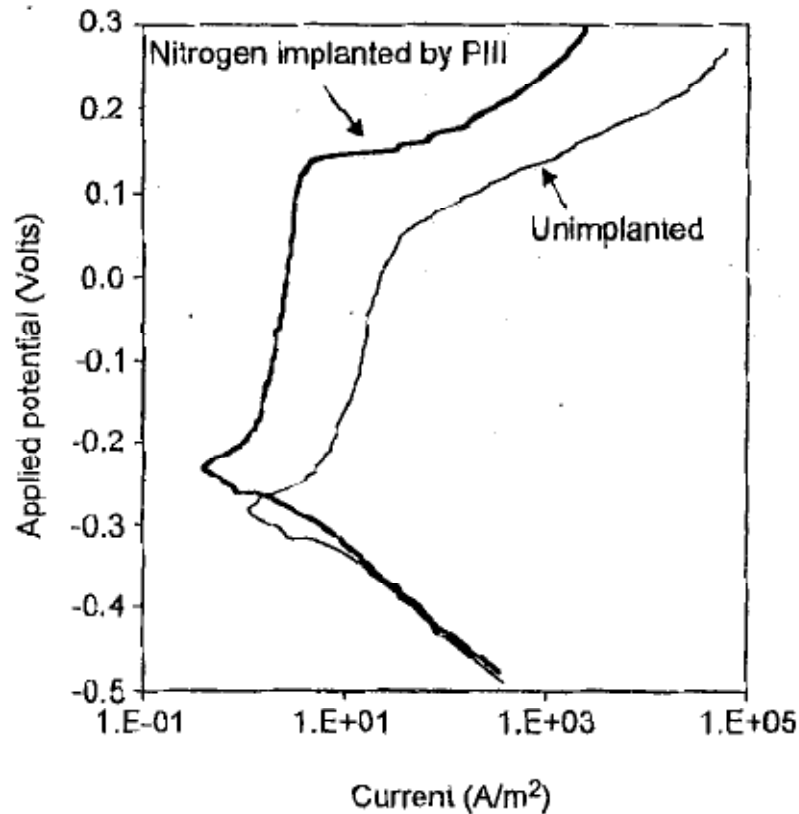


~ 2.5' diameter x 3' length



Nitrogen plasma

Nitrogen ion implantation of 17-7PH stainless steel (with Alison Gas Turbines)



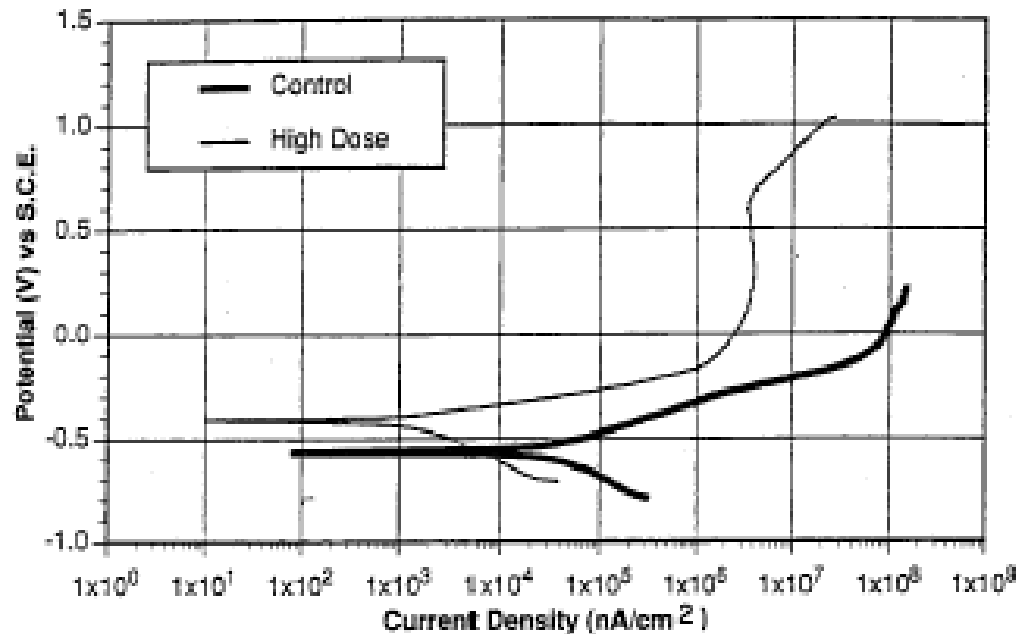
Corrosion testing in 3.5% NaCl solution; lower corrosion current and higher pitting potential

Also a 11% decrease in erosion rate for the N^+ implanted sample (compared to the as-received sample) under an accelerated test 90 mesh alumina powder at 20psi at 30° incidence

Corrosion and erosion tests performed at Alison Gas Turbines, IN



Nitrogen ion implantation of Cr-plating (in collaboration with Rock Island Arsenal, IL)



Improvement in wear resistance was also observed in pin-on-disk wear tests due to the formation of hard CrN phase

Corrosion testing in 3.5% NaCl solution; lower corrosion current due to the formation of CrN



PIIID surface modification for gyroscope bearings for Navy (with Kearfott Guidance & Navigation)

Bearings (~ 3mm dia.) made of AISI 52100 Bearing Steel

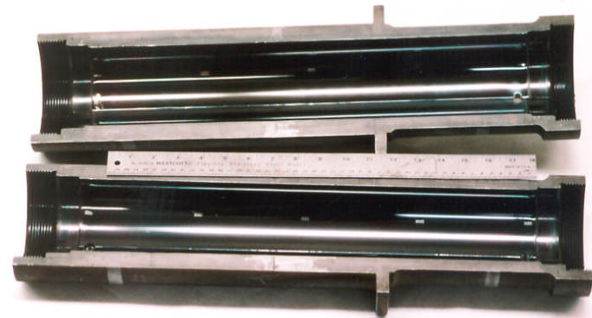
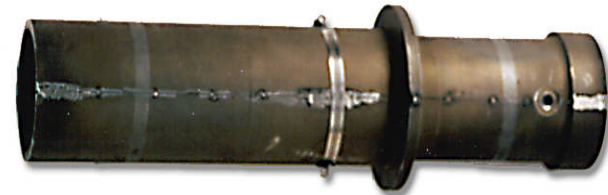
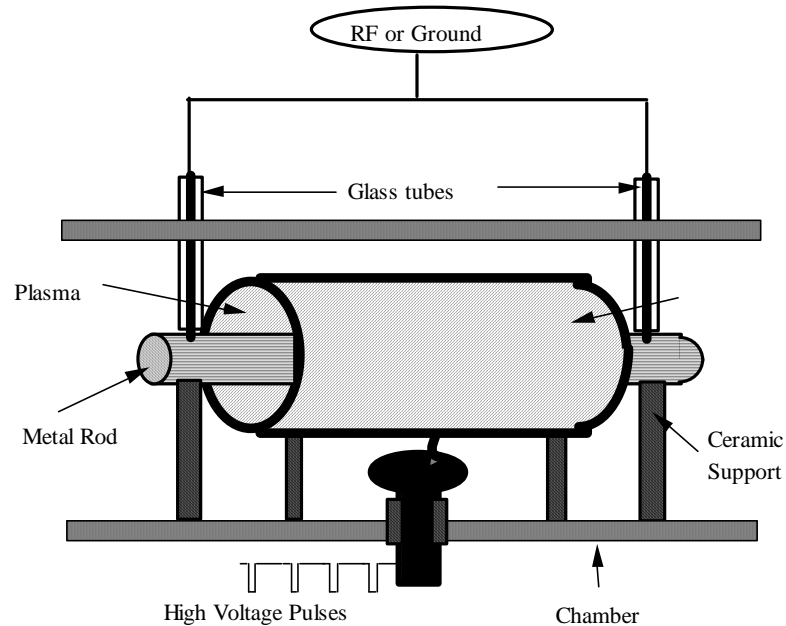
Goal to improve wear and rust resistance

**Carbon ion implantation with methane plasma: SIMS and Auger
depth of surface modification: ~120nm**

Test	Untreated 52100 steel	C ⁺ implanted
Wear scar after 4-ball wear test (0.65 max Mil. req.) (ASTM-D-4172)	0.69mm	0.32mm
Humidity test 14 day/90F/75 %RH	Rust observed (SEM 200x)	No rust



Deposition of coatings inside of tubes to reduce wear and oxidation (with Rock Island Arsenal, IL)



Diamond-like carbon (DLC) coating deposited on the inside surface of a cylinder (3.5" ID x 18" L) using acetylene plasma

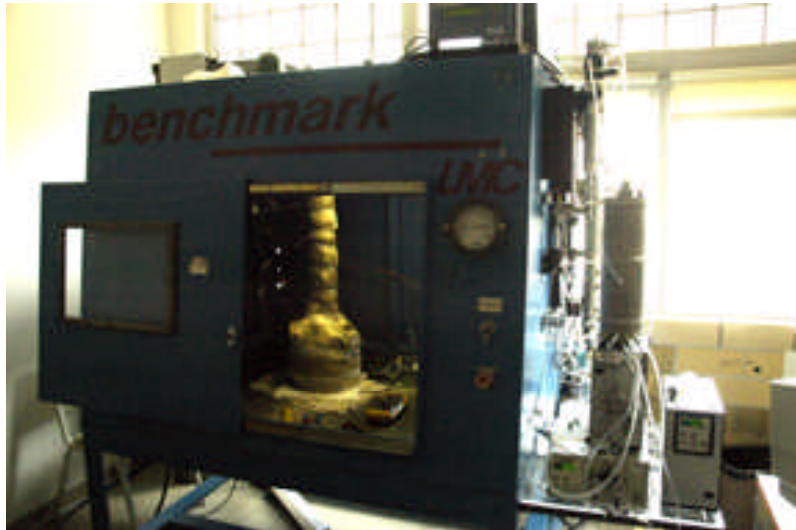
High temperature corrosion: Supercritical Water

Supercritical water:

- Water at temperatures greater than 374°C and pressures greater than ~ 3600psi
- Being considered for coolant for nuclear reactors and has been used in fossil fuel power plants for decades
- Very corrosive
- Has been investigated by the Army for toxic waste disposal [Dr. Robert Shaw, U.S. Army (ret.) will give a talk on this topic at the March 2009 NACE conference]

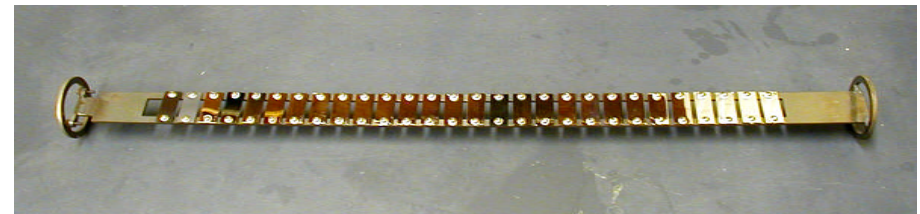


University of Wisconsin supercritical water corrosion testing system



Temperatures: Up to 600°C

Exposure times: Up to 3000 hours
(~ 4 months)



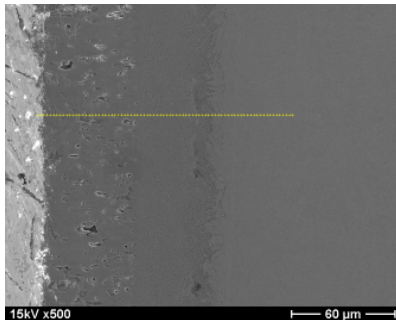
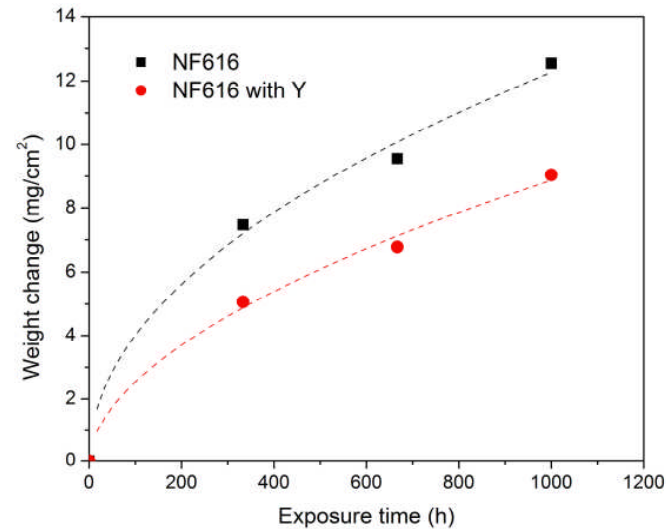
Sample Dimensions: 1.25"
length, 0.5" wide and ~0.02"
thick

Alloys studied include a wide
range of high temperature ferritic
and austenitic steels and
superalloys (625, 718 etc.)

Novel Approaches – Surface Treatments

600°C SCW exposure (NF 616 9% Cr ferritic steel)

Yttrium surface treatment
reduces the thickness of the
oxide layer formed on ferritic
steel

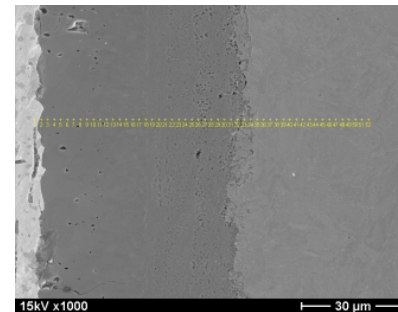


96 µm

NF616 after 6 weeks in 600°C
SCW (taken at 500x)



~ 44%
Improvement



53 µm

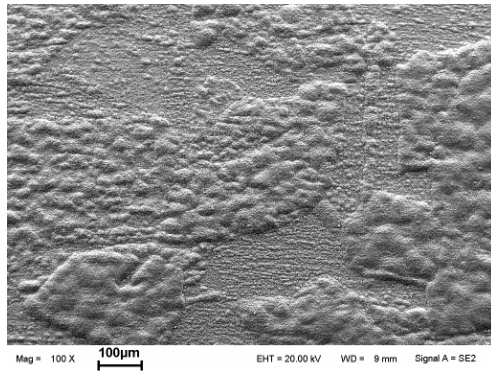
Y-surface treated NF616 after 6 weeks
in 600°C SCW (taken at 1,000x)



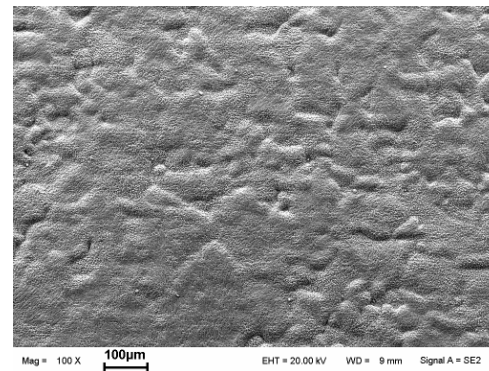
Novel Approaches

Grain Boundary Engineering e.g. Incoloy 800H

- Grain Boundary Engineering (GBE) to address oxide spallation in austenitic steels:
 - A combination of deformation and annealing steps, that enhances the population of low energy grain boundaries
 - Incoloy 800H is a high temperature ASME code certified alloy used in fossil and nuclear power industry



Alloy 800H after 6 weeks exposure in 600°C SCW



Alloy 800H after 6 weeks exposure in 600°C SCW



High temperature corrosion: Molten Salts

Molten Salts:

- Excellent heat capacity and thermal conductivity
- Used for storing solar energy, and transport of process heat from a nuclear reactor for hydrogen production
- Very corrosive
- At Wisconsin research has been performed on high temperature fluoride and chloride salts and low temperature nitrate salts
- In the 1950s the Army, under the Aircraft Reactor Experiment program, tested nuclear powered aircraft using U-fuel dissolved in molten salts)



Experimental system for evaluation of corrosion in molten salts

Graphite crucible

Graphite central rod for fixturing samples

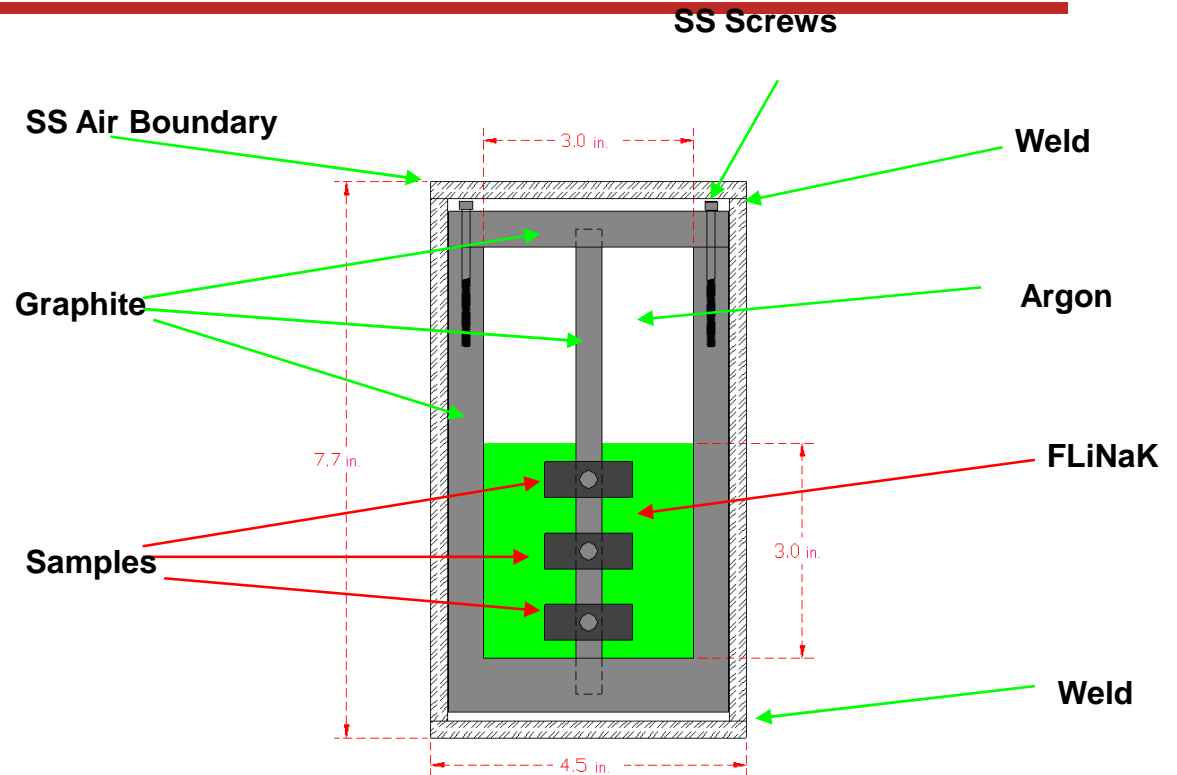
Stainless steel outer shell for additional purity and safety

One crucible/alloy/test

Alloys tested in triplicate

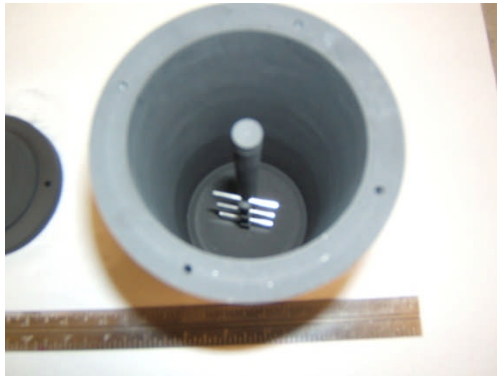
Minimal interfaces between materials and environment

Argon space large enough for FLiNaK when flipped for sample retrieval

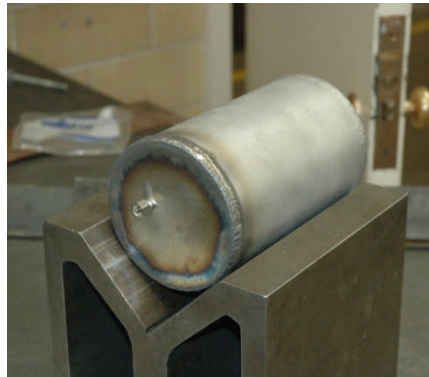


Test Conditions: 850°C for 500 hr

Procedure for preparation of corrosion capsules



Graphite capsule with samples



Capsule welded and ready for molten salt introduction



Salt transfer apparatus in glove-box



Cutting the capsule

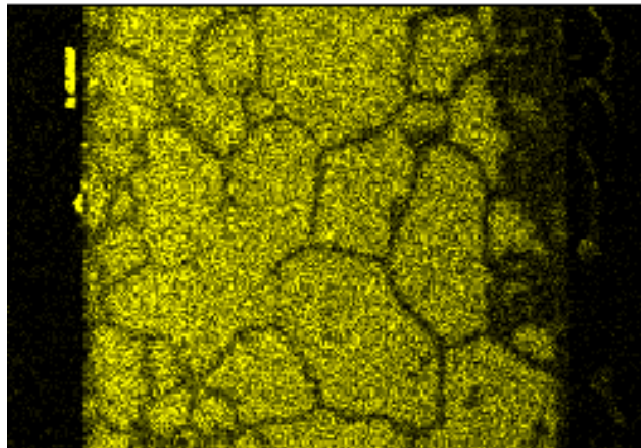
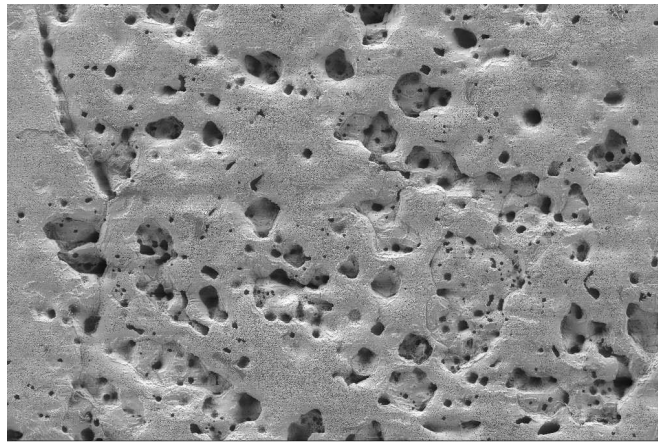


Salt drained away from the samples

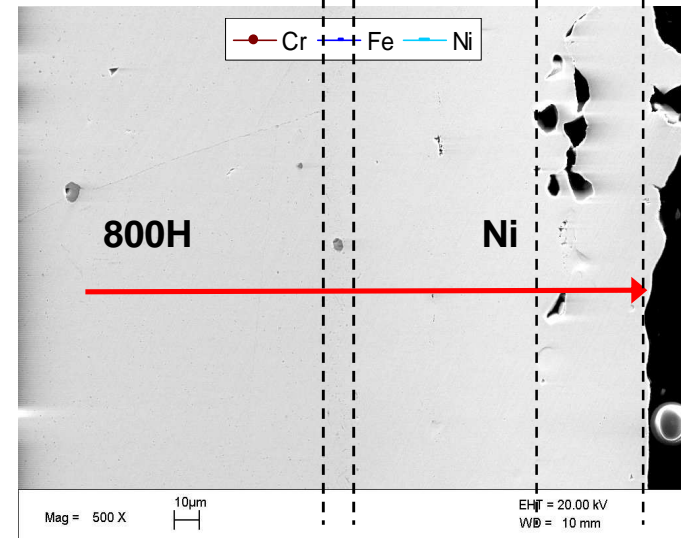
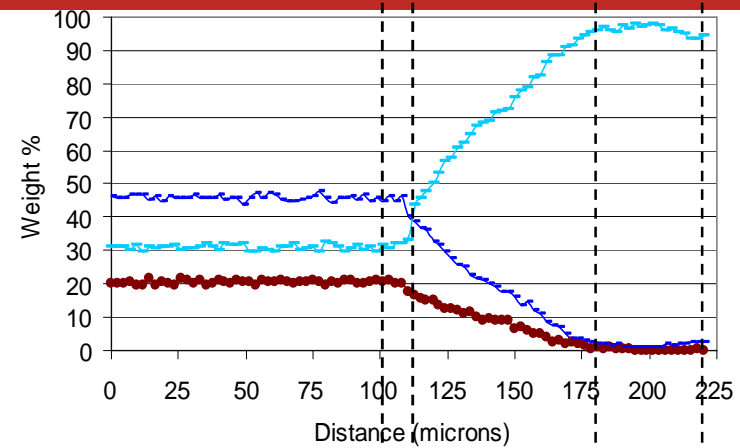


Graphite central rod with samples removed from corrosion cell

Corrosion of Incoloy 800H (20% Cr) and Ni electroplated Incoloy 800H in Na/K/Li fluoride salt: Ni coating greatly mitigates corrosion



Incoloy 800H



Ni electroplated Incoloy 800H

Concluding Remarks

- Corrosion research at the University of Wisconsin is focused on two areas (i) plasma-based surface treatments to reduce corrosion, (ii) high temperature corrosion in harsh environments
- Plasma-based surface treatments (10 to 2000nm depth) have involved ion implantation and thin film deposition and atomic mixing approaches to mitigate corrosion and wear
- Specific testing equipment for corrosion testing in high temperatures and harsh environments such as supercritical water, molten salts, supercritical carbon dioxide (KAPL), and helium have been designed and built
- Room temperature corrosion tests for potentiodynamic corrosion tests, impedance spectroscopy, and salt spray test facilities exists and are being used for research in conjunction with a suite of materials characterization techniques
- Research projects involve the development of a basic understanding of corrosion mechanisms as well as strategies such as surface treatments and grain boundary engineering to mitigate corrosion

